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Surface Segregation of Tackifier in Pressure Sensitive Adhesives

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13. ABSTRACT *(Maximum 200 words)*

The project as finally funded was cast in the form of a proof-of-concept study with a narrow focus. The objective was to demonstrate the feasibility of characterizing tackifier concentration depth profiles in pressure sensitive adhesive films and correlating these profiles with adhesive performance. Thin films of isoprene and mixed with various amounts of an abietic acid ester tackifier were studied using a combination of neutron reflectometry (NR), forward recoil spectroscopy (FRES), x-ray reflectometry (XR) and ellipsometry (EL) to provide unprecedented spatial resolution of the near surface profile.

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Specific Aims:

The project as finally funded was cast in the form of a proof-of-concept study with a narrow focus. The objective was to demonstrate the feasibility of characterizing tackifier concentration depth profiles in pressure sensitive adhesive films and correlating these profiles with adhesive performance. Thin films of isoprene and mixed with various amounts of an abietic acid ester tackifier were studied using a combination of neutron reflectometry (NR), forward recoil spectroscopy (FRES), x-ray reflectometry (XR) and ellipsometry (EL) to provide unprecedented spatial resolution of the near surface profile.

Results from proof-of-concept study

A model tackifier, n-butyl ester of abietic acid and a deuterium labelled analog were synthesized, purified, characterized, and used to make model adhesive thick (bulk-like) films with polyisoprene elastomer (ca. 300,000 molecular weight). The bulk miscibility, glass transition temperature, rheology and probe tack of model adhesive mixtures of several composition have been surveyed. The ester tackifiers are oils, in contrast to typical commercial rosin-based tackifiers. However, they still provide a tackifying action. The tackifier and PI are miscible in the bulk and one finds a single glass transition temperature (T_g) for tackifier compositions up to 70 wt% with T_g increasing with tackifier concentration. Dynamic mechanical thermal analysis results show a decrease in modulus at low frequency and increase in modulus at high frequency. Thin films and surfaces of a few mixtures have been studied by FRES, NR, XR, probe tack and contact angle measurements. Study of thin films spun cast onto polished silicon wafers show an interesting dependence of wetting and film stability on antioxidant content, wafer surface character, and film thickness. Stability of a film to dewetting improves with addition of antioxidant and increased film thickness. Surveying this behavior in order to avoid unstable films was an unexpected, but necessary component of the study.

"Unannealed" films of ca. 1900 Å thickness for NR and FRES analysis were spun cast onto polished silicon wafers cleaned in a manner to preserve the native oxide layer. This thickness allowed study of the concentration profile at both the film/air and film/substrate interfaces. Two comparable films containing 15wt% tackifier analysed by NR and FRES are discussed here. Each was allowed to remain at room temperature in the dark for at least 18 hrs prior to the measurement.

FRES data were collected at the ion accelerator facility in the Materials Science Research Center at Cornell University, using a low resolution beam line. The sample was measured with a cold stage at liquid nitrogen temperature to avoid ablation of the tackifier. That deuterated tackifier is present in the film was readily seen in the FRES data. The FRES measurement also clearly indicated that segregation to both interfaces must be reasonably subtle. That is, the surface excess, $z^* \left(= \int_0^\infty [\phi(z) - \phi_\infty] dz\right)$ at each interface must be less than about 40 Å. The use of NR was necessary to resolve the fairly thin enrichment layers which exist at both interfaces.

The NR measurement was performed at room temperature on the fixed wavelength (λ = 2.35Å) reflectometer on beam tube seven at the National Institute of Standards and Technology NBSR research reactor. In this very first measurement, data were not taken for as large a range of values of scattering vector,q, as will be typical of later measurements. (This subquently limits the resolution in this particular data). The data, shown in Figure 1, was corrected for background and the effect of varying slit size before being analyzed using established procedures. Parameters describing the film's concentration profile were determined by optimization of the agreement between the experimental data and a simulated curve derived from a candidate composition profile. The enrichment layers at the air and substrate interfaces had thicknesses of 130±7 and 150±7 Å, respectively.

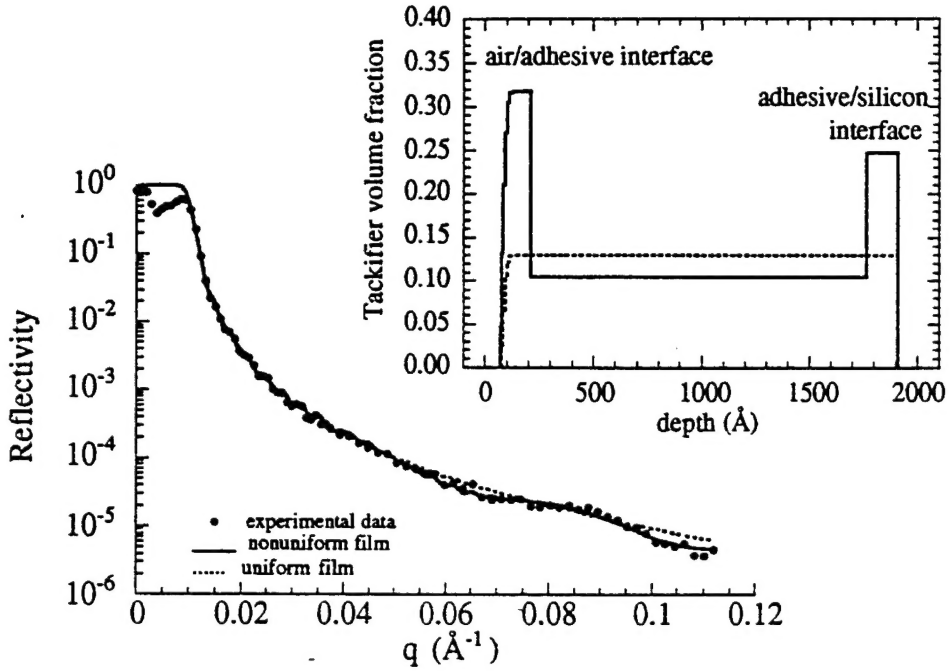

Figure 1. Comparison of the NR data (dots) from an annealed sample with 15wt.% tackifier with simulated curves for the two models shown in inset. The film composition is clearly not uniform, and in fact segregation is seen at both interfaces.

Values of probe tack measured on thicker films (ca. 0.4 - 0.5 mm) supported on Si wafers were provided as a gift of James Miller of Chemsultants, International, and are summarized in Figure 2. This preliminary data suggest that a maximum in tack occurs at a concentration somewhat less than that at which the water contact angle stops changing. One may imagine that the optimal adhesion properties are seen at a bulk concentration less than that necessary to saturate the surface with tackifier.

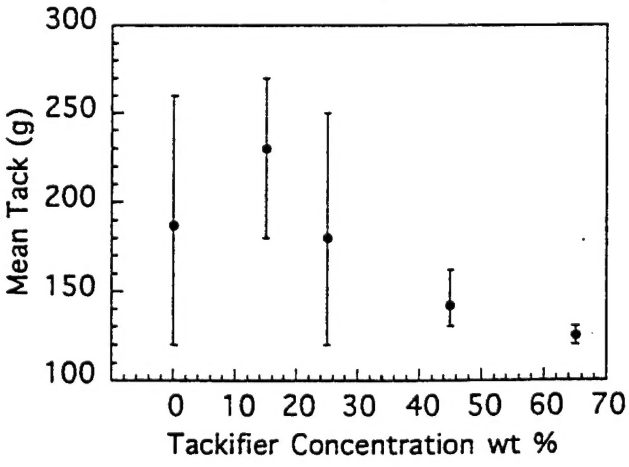

Figure 2. Variation in Polyken probe tack results (ASTM D2979) with tackifier concentration from triplicate measurements at each concentration. Contact time = 1 sec. Initial probe tack measurements suggest a maximum at a loading in the neighborhood of 15 wt%.

Significance of results

These measurements demonstrate the application of FRES and NR to the characterization of pressure sensitive adhesives for the first time and confirm the sensitivity of these two techniques to the tackier composition profiles of interest. Such characterization will play an important role in establishing the relationships between adhesive structure and performance which are necessary for the rational design of superior adhesives for army use. A model adhesive with a hydrogenated PI matrix, which has better temperature stability than does PI, will be investigated next.